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STRUCTURE/PROPERTY STUDIES OF A HETEROCYCLIC CONDUCTIVE
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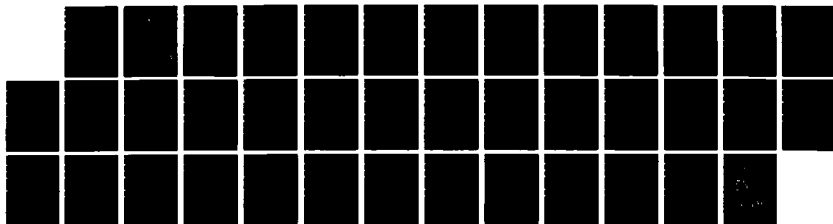
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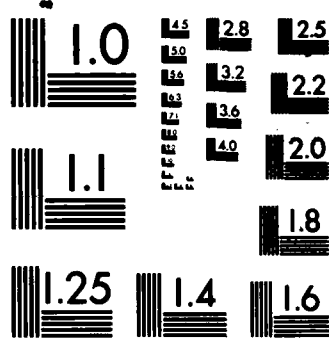
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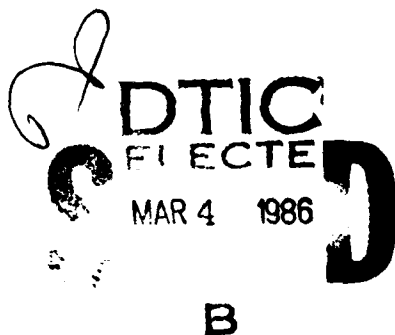
STRUCTURE/PROPERTY STUDIES OF A
HETEROCYCLIC CONDUCTIVE POLYMER

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19. ABSTRACT (Continued)

X-ray and electron diffraction were used to study the film morphology and the x-ray results indicate a non-homogeneous structure. Reflection and transmission x-ray diffraction show a difference in d-spacing and order exists perpendicular and parallel to the plane of the film. D-spacings for the low-angle peaks correspond to the Van Der Waals size of the anion. Correlations between macroscopic properties and polymer/anion structure are addressed.

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INTRODUCTION

The potential benefits of an electrically conductive polymer consist of the possibility of combining the attractive characteristics of polymers such as low density, processing variability, and reasonable environmental stability with the electrical properties of a semi-conductor or metal. These materials possess an enormous potential as possible candidates for use in lightweight batteries, polymeric electromagnetic shielding components, photovoltaic cells, electrodes, and electronic switches. In principle, the well-established ability to tailor a polymer for a specific set of physical and mechanical properties is now broadened to include electrical behavior.

The usefulness of electrically conductive polymers has been limited by either the lack of environmental stability, inherent processing constraints, or poor mechanical behavior. While an extensive effort has been directed towards synthetic chemistry and electrical properties, few studies have focused on structure/mechanical behavior relationships [1-5]. However, utilization of such materials will depend on understanding the mechanical behavior based on the chemical structure along with understanding the physical behavior.

This study is directed at defining and understanding the role of the dopant species in the mechanical behavior of several polypyrrole/dopant anion systems. Conductive polypyrrole has exhibited creditable environmental stability with minimal conductivity losses upon exposure to the atmosphere [6]. Although it is intractable, the noteworthy mechanical integrity of Polypyrrole has prompted continued interest in its study for potential electronic applications. Conductive polypyrrole is actually a composite on a molecular level with an ionic attraction between polymer and dopant species. Understanding the relationship of this structure to the material behavior may aid in controlling the strength, compliance, and energy-absorbing characteristics (toughness) of the material.

STRUCTURE/PROPERTY STUDIES

Of the many structure/property studies undertaken in conductive polymers, the majority of these efforts have been on polyacetylene or polyacetylene blends [1-3, 7-10]. The characterization usually consists of one or more types of spectroscopy (such as IR, UV-VIS, NMR, XPS, etc.) in addition to thermal analysis, electrical conductivity, and diffraction studies. Heterocyclic conductive polymers such as polypyrrole and polythiophene have also been studied extensively. Pfluger and Street have used XPS to characterize the chemical and physical properties [11]. In this study XPS techniques were used to investigate the structural disorder in polypyrrole and polybithiophenes grown electrochemically. Nazzari and Street have used radiochemical technique to determine the molecular weight of pyrrole-based polymers [12]. The results showed that the average number of pyrrole units was about 750 for polydimethylpyrrole perchlorate which corresponds to a molecular weight of about 100,000. However, the molecular weight of polypyrrole itself may be significantly different in view of the potential role of the beta-carbons in chain branching. X-ray diffraction studies by Wegner have been used to derive a structural model of polypyrrole with various alkyl-sulfonates. In addition, there have been numerous other studies on the chemical structure and physical properties [13-16].

The mechanical properties have not been addressed as extensively. Diaz and coworkers have reported on the effects of the preparation conditions on the mechanical behavior [4]. Their results indicate a change in conductivity and tensile strength with electrolyte solvent. Wynne and Street have examined the mechanical behavior of polypyrrole while improving the synthetic procedure [17]. In this study it was found that polypyrrole could be grown on vitreous carbon electrodes

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which allow the use of high voltages and high currents to permit the growth of thick films in relatively short times. Ogasawara et al., have obtained improved strain to failure and increased electrical conductivity via various preparation conditions. [18].

EXPERIMENTAL

MATERIALS

An electrolytic cell was used in the synthesis of the polypyrrole/anion films. Two sizes were employed. One was a 200 ml capacity beaker with a vitreous carbon anode (Atomerich Chemetals) and a platinum mesh cathode that produced approximately 18 cm² of polymer film. The larger cell consisted of a 2.0 liter capacity battery jar with vitreous carbon and platinum mesh electrodes that produced approximately 75 cm² of film. An Ag/Ag⁺ (Ag in 0.1M AgNO₃ and acetonitrile) reference electrode was used to determine the potential. This reference electrode was checked against a standard calomel electrode and showed a 0.345 V potential difference. This value fell within the range of 0.28 to 0.35 V reported in the literature [19]. All of the syntheses were performed under constant potential while monitoring the current density. In addition all of the syntheses were performed under ambient conditions (23°C and approximately 60% RH).

The polypyrrole films were prepared according to the method developed by Wynne and Street for production of PP/OTs films without special precautions to exclude air [17]. The cell solution consisted of pyrrole (0.3M), the dopant species (0.15M), and acetonitrile. The pyrrole was passed through 300 mesh activated alumina prior to use. Spectral grade acetonitrile was used without further purification. The tetraethylammonium p-toluene sulfonate (OTs) and silver p-toluene sulfonate were used as received (Alfa). A small amount of water (0.5%) was added to the solution to provide the cathode reaction which is the reduction of protons.

Other para-substituted benzene sulfonates were synthesized for use as the dopant counterion. In each case, the acid was mixed with tetraethylammonium hydroxide (TEA-OH) on a 1:1 molar basis. The TEA-OH is supplied as 40% in solution with water. For example, 42.8 ml (0.283 moles) of ethylbenzenesulfonic acid was reacted with 100 ml (0.283 moles) of tetraethylammonium hydroxide (40% in water) in a stirred flask. To remove the water and isolate the salt the compounds were placed in a large evacuated dessiccator with P₂O₅. The purity of the product salt was examined by proton NMR. The tetraethylammonium salts of benzenesulfonate (BS), ethylbenzenesulfonate (EBS), and dodecylbenzenesulfonate (DBS) were made in the above manner. For the perchlorate films the lithium salt was used as received. These films were prepared in tetrahydrofuran under dry box conditions [20].

COMPOSITION AND PHYSICAL STUDIES

Elemental analyses were performed on samples that were extracted in a soxhlet apparatus for a minimum of 4 hours and dried at 95°C under dynamic vacuum for 8 hours. The analyses were performed by Schwarzkopf Laboratories. Electrical conductivity was determined by a four-point probe technique as described by Wieder [21]. If t (sample thickness) $\ll S$ (probe spacing) then the sample may be considered as essentially two-dimensional and the following equation may be used.

$$\frac{1}{\sigma_e} = \rho = \frac{v}{i} \frac{\pi t}{\ln 2}$$

ρ = resistivity

v/i = resistance

The flotation densities were measured using a density gradient column of CCl₄ and toluene with a calibrated range of 1.35 to 1.38 g/cm³. The column was prepared in the following manner. The high density solution was formed from a mixture of 200 ml of CCl₄ and 800 ml of toluene with a resulting density of 1.446 g/cm³. The low density solution was formed from a mixture of 400 ml

CCl_4 and 600 ml of toluene with a resulting density of 1.302 g/cm^3 . After attaining hydrostatic equilibrium, the solutions were slowly allowed to fill the column simultaneously to form the density gradient. The column-filling procedure took 4 hours. Thermogravimetric analysis (TGA) was performed with the DuPont 1090 system at a heating rate of 10°C/min . with atmospheres of nitrogen or air.

MECHANICAL BEHAVIOR

The mechanical behavior was assessed by determining the tensile strength, strain to failure, and modulus using an Instron test machine. A strain rate of $.05''/\text{min}$ was used. Air grips were employed to prevent slippage. The testing was performed at 23°C . Dynamic mechanical tests were run using the DuPont 982 DMA with 1090 control system and an automated (IMASS) rheovibron. The heat-up rates of these systems were 5°C/min and 1°C/min respectively. The DMA from DuPont measures the power necessary to maintain the resonant frequency of the sample as the temperature changes. The stress state is complex and the frequency is constantly changing with temperature. In the rheovibron a sinusoidally varying tensile strain is applied to one end of the sample and the resulting stress response is measured. The frequency remains constant while the temperature changes. To assume a linear viscoelastic response the amplitude of the strain is kept small. The rheovibron was run at frequencies of 11 and 110 Hz.

DIFFRACTION STUDIES AND MICROSCOPY

Electron diffraction was performed on polypyrrole samples that were ion milled at liquid nitrogen temperatures. The optimum thickness is between 500 and 1000\AA and can be achieved by slowly (48 hrs.) milling the sample until penetration and then using the thinned sample near the hole. The conductive nature of the samples in addition to their intractibility decrease the possibility of degradation of the material. A Joel 200CX electron microscope was used at 200 kV for the electron diffraction and transmission electron microscopy (TEM) studies.

X-ray diffraction studies were performed on as-prepared samples in the reflection and transmission modes. Wide angle x-ray scattering (WAXS) and small-angle x-ray scattering (SAXS) were used to study each of the materials. The equipment consisted of a TEC 210 proportional counter, Picker x-ray, Ortec power supply, and Lecroy 3500 minicomputer.

RESULTS AND DISCUSSION

Coupling the behavior of a polymeric material to its structure and morphology requires definition of the critical issues to be addressed. In this study the polymer is actually a composite of polypyrrole and the anion species, of which the latter may be present in substantial quantity. It therefore follows that the concentration of the anion as well as the size or shape may be significant in determining structure/property correlations. Control of the structure through variations in the synthesis may ultimately provide the desired properties. The following sections will present experimental results and discussion relevant to these issues.

COMPOSITION AND CHARACTERIZATION

Elemental analysis was performed on PP^+/OTs^- films prepared at several electrode potentials to investigate the possible influence of potential on polymer/dopant compositions. Table I contains the first set of elemental data for potentials that ranged from 0.54V to 1.2V vs the Ag/Ag⁺ reference electrode. Oxygen was determined by difference. The sulfur/nitrogen (S/N) ratio was found to increase with synthesis potential. A second set of data was generated on additional samples made with high and low synthesis potential to check the previous results. These data, also given in Table I, show the same trend which is the S/N increase with potential. A third set of data (see Table I), using silver tosylate, indicated no "entrapped" salt (i.e., no silver was found in the films) and showed the same relationship of increasing S/N with increasing potential. The S/O ration remained fairly constant for all of the samples. These results indicate the possibility of an increase in the anion concentration as the synthesis potential is increased.

Diaz and coworkers have reported a S/N ration of 0.32 for PP^+/OTs^- prepared at potentials of 0.8 to 1.3V vs. the saturated sodium calomel electrode (SCC) [4]. This corresponds to 0.46 to 0.96V vs. the Ag/Ag⁺ electrode in which the S/N ratio was greater (0.37 to 0.40). The films with the lower S/N ratio were removed from the electrode, rinsed with acetonitrile, and dried in air. Therefore, it is possible that residual acetonitrile remained in the samples causing a lower S/N ratio. Street et al. reported a S/N ratio of 0.43 for PP^+/OTs^- films prepared at an applied potential of 3V [5]. These films were dried in dynamic vacuum at 95°C.

The flotation densities of the first set of PP^+/OTs^- films (0.54V to 1.20V) were measured and were found to decrease as the potential increased. The data support the notion of an increase in anion concentration with synthesis potential which will distort the structure and decrease the density.

Other dopant counterions were used in this study and are shown in Figure 1. The benzene (BS), ethylbenzene (EBS), and dodecylbenzene (DBS) derivatives were chosen to compare other para-substituted benzene sulfinates with toluenesulfonate (OTs). The biphenylsulfonate was also attempted but failed to yield films of adequate mechanical integrity for further testing. Perchlorate films were also studied.

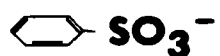
The electrical conductivity of each polypyrrole/anion system was measured via a 4-point probe apparatus and indicated small differences with respect to the dopant anion. No significant conductivity differences were noted for OTs films prepared at different potentials. Literature values for PP^+/OTs^- are approximately 100 (OHM-CM)⁻¹. Recent studies have addressed the stability of the electrical conductivity of polypyrrole/anion systems at ambient and elevated temperatures [22, 23]. In the first study, Munstedt and coworkers show the influence of various comonomers and counterions on the conductivity [22]. The polypyrrole with benzenedisulfonicacid showed

TABLE I. ELEMENTAL ANALYSIS DATA FOR PP+OTS-

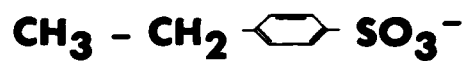
<u>E_{APP} (V)</u>	<u>E_{REF} (vs. Ag/Ag⁺) (V)</u>	<u>$i \left(\frac{\text{mA}}{\text{cm}^2} \right)$</u>	<u>S/N</u>	<u>S/O</u>	<u>C/H</u>
3	0.54	1.00	0.37	0.28	1.06
4	0.79	2.72	0.39	0.29	1.08
5	1.09	4.81	0.42	0.28	1.07
6	1.20	7.44	0.51	0.28	1.03
3 II	0.54	0.51	0.37	0.24	1.01
6 II	1.20	3.61	0.44	0.26	1.02
1 (Ag)	0.24	--	0.42	0.26	1.04
3 (Ag)	0.63	--	0.49	0.26	1.01



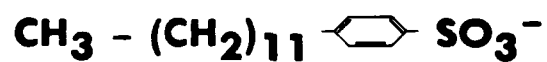
P - TOLUENESULFONATE (OTs)



BENZENESULFONATE (BS)



ETHYLBENZENESULFONATE (EBS)



DODECYLBENZENESULFONATE (DBS)



PERCHLORATE

Figure 1. Counterion Chemical Structures.

the highest stability with a 50% drop in conductivity at 140°C in 150 days for benzenesulfonic acid, 1.4 days for ClO_4^- , 15 days for BF_4^- , and 1.9 days for PF_6^- . In the other study, Druy and coworkers found PP^+/OTs^- to be intrinsically stable with respect to conductivity loss in an inert atmosphere [23]. This was the first conducting polymer to make that claim. Activation energies from that study predict a loss of one decade in conductivity for a 3-year ambient exposure period. PP^+/OTs^- was also shown to be thermally stable up to 150°C (in an inert atmosphere) with respect to conductivity loss and only 35% loss at 200°C for 16 hours. It is evident from both of these studies that the dopant anion can influence the environmental stability of the polymer.

MECHANICAL BEHAVIOR

Compositional effects on the ultimate tensile strength were investigated for PP^+/OTs^- at each potential. The tensile strengths were determined at room temperature and indicate a loss in strength with increasing synthesis potential or S/N ratio (see Figure 2). If the increase in S/N ratio represents an increase in anion content corresponding to an increase in oxidation of the polypyrrole, then the loss in strength is due to the incorporation of more anions within the polypyrrole/anion structure. An effect due to current density was also observed. At the lower density (0.51 mA/cm^2 vs. 1.0 mA/cm^2) the ultimate tensile strength was approximately 30% higher. The same relationship has been noted for polybithiophene/perchlorate where films electrochemically grown under lower current densities tended to have superior mechanical integrity [48]. The ultimate tensile strength was also found to decrease with other dopant anions. A summary of the ultimate tensile strength, tensile modulus, and strain to failure is given in Table II. Note the difference between PP^+/OTs^- (dry) which was prepared in a dry box. The ultimate tensile strength was approximately the same but the modulus (tensile modulus) was higher and the strain to failure less than half. The plasticizing effect of moisture decreases the modulus and increases the strain to failure as shown in Table II. This same effect was seen by Street and coworkers for PP^+/OTs^- films which were dried before testing [5, 17].

The stress-strain behavior was determined by taking the average of 14 samples for the ultimate tensile strength and strain to failure and then using a sample that most closely represented the average to determine the stress-strain curves. The data in both cases show no distinct yield point but rather a smooth elastic-plastic transition. This same behavior was noted by Street and coworkers [17]. The ultimate tensile strength, tensile modulus, and strain to failure are decreased for PP^+/DBS^- as well as for all of the other dopant anions compared to OTs (see Figure 3). In this figure the best attainable materials are compared. The PP^+/DBS^- and PP^+/BS^- samples were prepared in the small cell arrangement at a potential and current density that yielded films with the best mechanical integrity. Attempts to prepare these films at lower potentials and current densities yielded very thin, brittle films unsuitable for further testing. The preparation current densities of PP^+/DBS^- and PP^+/BS^- are higher than that of PP^+/OTs^- prepared in the larger cell arrangement. Using the data of Figure 2 (PP^+/OTs^- made in the small cell) the ultimate tensile strength of PP^+/DBS^- is approximately the same as PP^+/OTs^- while that of PP^+/BS^- is slightly lower (7%). The dry OTs^- and ClO_4^- samples were made with the larger cell (lower current density) and consequently show higher ultimate tensile strengths compared to the materials made in the smaller cell (higher current density). This significant effect due to the preparation conditions may explain the rather wide range of ultimate tensile strength values given in the literature and in this study. For an equal comparison of PP^+/OTs^- and PP^+/DBS^- with respect to synthesis potential and current density, the stress-strain curves are given in Figure 4. Note the ultimate tensile strengths are approximately equal.

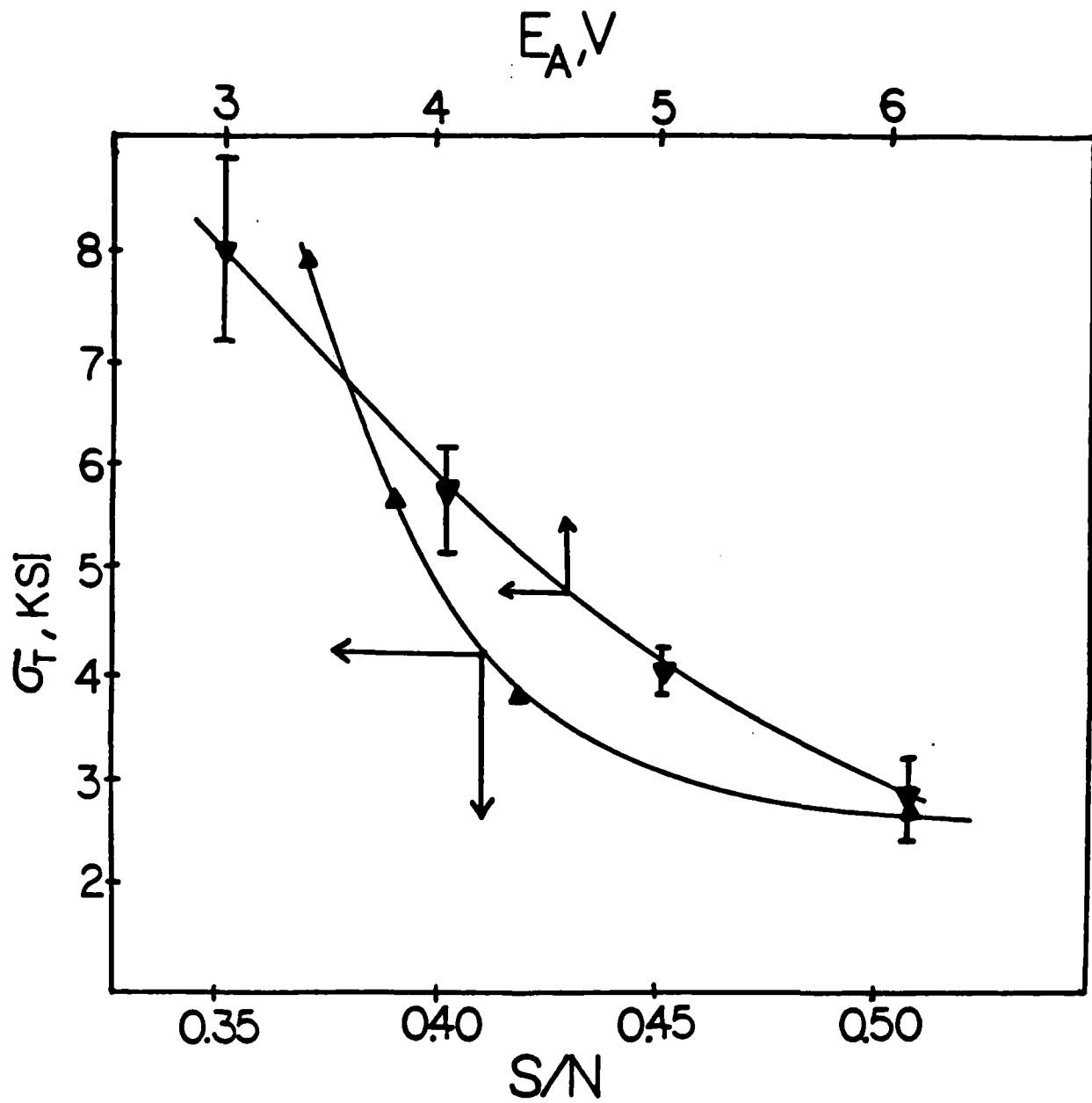


Figure 2. Plot of Ultimate Tensile Strength vs. E_{App} and S/N Ratio.

TABLE II. SUMMARY OF MECHANICAL PROPERTIES

<u>MATERIAL</u>	<u>σ_{UTS} (PSI)</u>	<u>E_T (PSI)</u>	<u>ϵ_F</u>
PP/OTs	10589	2.08×10^5	0.27
PP/OTs (DRY)	10227	2.35×10^5	0.128
PP/CIO ₄	9220	1.60×10^5	0.22
PP/BS	5181	1.60×10^5	0.081
PP/DBS	6072	1.24×10^5	0.092

Stress-Strain Data

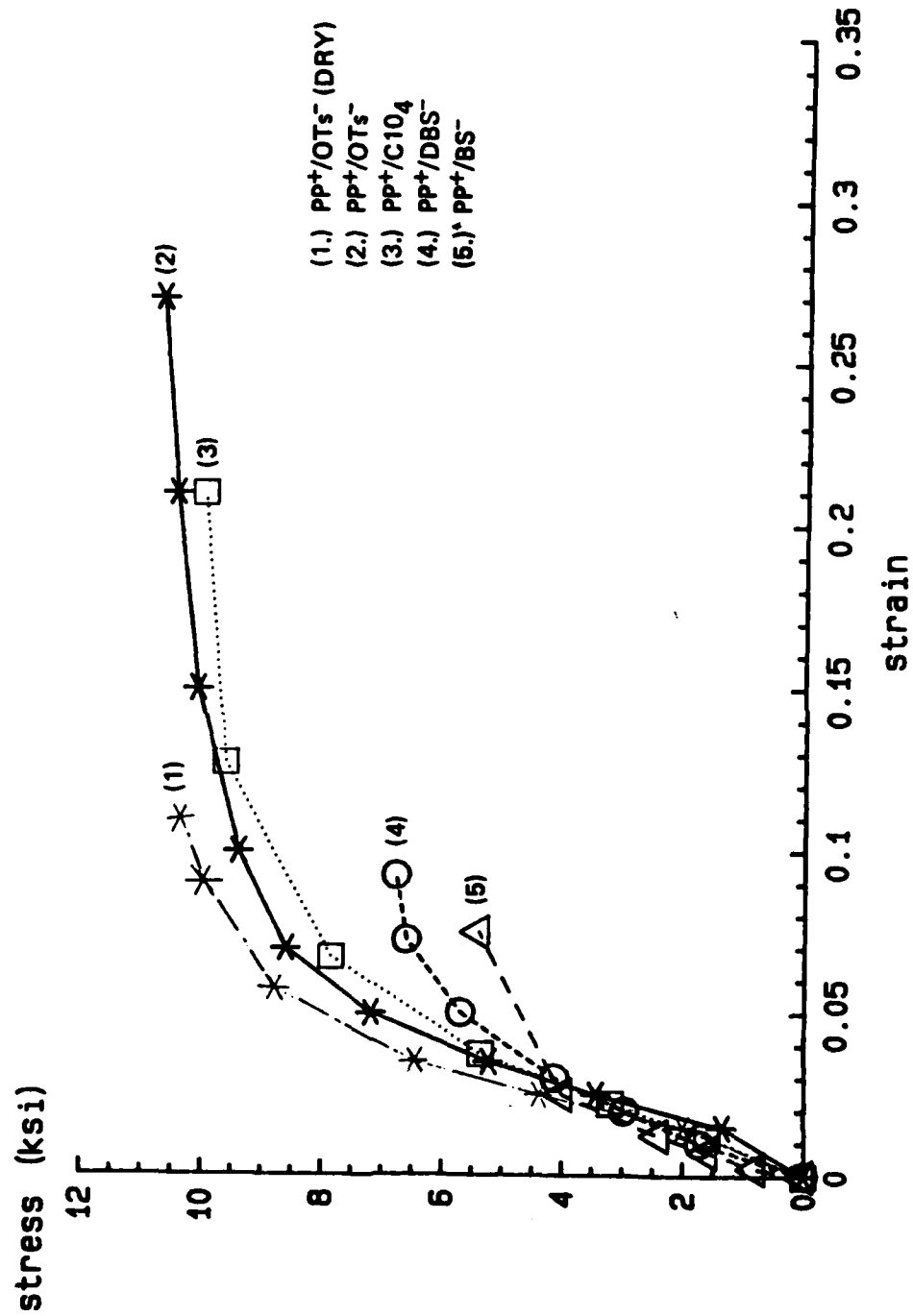


Figure 3. Stress - Strain Plots for Polypyrrole/Anion Systems.

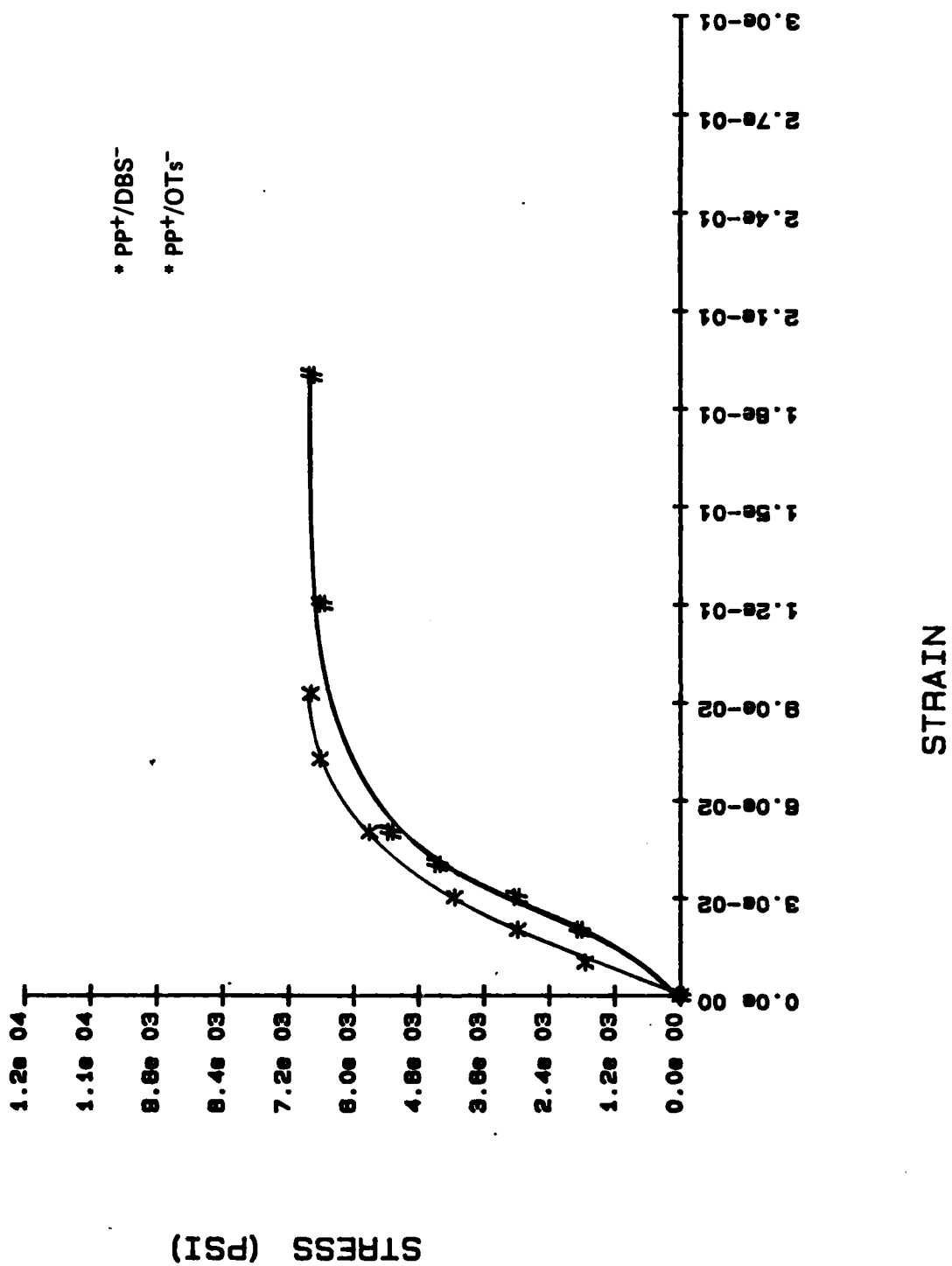


Figure 4. Stress — Strain Plots of PP+/OTs- and PP+/DBS- (Equal Current Densities and Synthesis Potentials).

The dynamic mechanical behavior of the PP^+/OTs^- films was studied by two independent techniques, the constant frequency rheovibron and the variable frequency DMA from DuPont. Examples are given in Figures 5 and 6. Both tests indicate a small transition in the storage modulus (E') at about 40°C . A broad peak in the loss modulus (E'') and $\tan \delta$ also occurs. This result was very consistent for the PP^+/OTs^- films and was not affected by the synthesis potential. This small transition was also not affected by the type of dopant anion. This behavior was repeatable and corresponds to the temperature at which all of the films were prepared. The relatively stiff structure of polypyrrole would indicate a glass transition temperature (T_g) much greater than 40°C . Therefore this small change in the modulus is not a T_g and resembles a secondary transition that is most likely due to a slight movement of a short segment of the polypyrrole backbone. In the high temperature rheovibron run shown in Figure 7 there is no indication of a true glass transition. Figure 7 shows the excellent thermal stability of the PP^+/OTs^- material. The storage (E') and loss (E'') moduli are not affected by temperature up to 230°C in air. This material withstands a relatively wide range of temperature (~ 150 to 230°C) without a large change in modulus and exists as a flexible film within the entire range.

STRUCTURE AND MORPHOLOGY STUDIES

Electron diffraction studies of several of the polypyrrole/anion systems showed the diffuse rings typical of amorphous polymers. The outer rings in the patterns give d-spacings of 1.1 and 2.2 Å and are most likely harmonics of the inner ring which gives a spacing of 3.2 Å. These results are close to the value reported in the literature by Geiss and coworkers for polypyrrole chains [24]. Discernible differences between the electron diffraction patterns of these amorphous polymers did not provide optimum information on chain spacings due to the diffuse nature and low contrast in the center of the pattern. Photometer readings did not aid in interpreting these results.

X-ray diffraction studies were performed in the transmission and reflection modes. In the reflection mode d-spacings perpendicular to the plane of the film are observed while in the transmission mode d-spacings parallel to the plane of the films are observed. A comparison of the reflection patterns for PP^+/OTs^- and PP^+/DBS^- is shown in Figure 8. Note that the lowest 2θ value is 7.5° degrees which was due to the geometrical constraint of the sample holder. The PP^+/OTs^- material exhibits a sharper peak at $2\theta = 25.778^\circ$ compared to each of the other PP/anion systems. This represents a greater degree of order which does not exist in the other systems. PP^+/OTs^- also exhibited the best mechanical behavior. The mechanical behavior of the $\text{PP}^+/\text{C10}_4^-$ system ranked second and correspondingly had the next sharpest peak at $2\theta = 25.143^\circ$. The x-ray data indicate the greater the degree of order the better the mechanical behavior.

Transmission x-ray data for PP^+/OTs^- is shown in Figure 9. Data collected down to $2\theta = 2^\circ$ shows a small-angle peak at $2\theta = 5.317^\circ$. The wide-angle peak was shifted to a lower 2θ value indicating a non-homogeneous structure (compared to the reflection data). Table III contains the d-spacings that correspond to each wide-angle peak for each of the materials in the reflection mode. The spacing of coplanar pyrrole rings is reported to be 3.41 Å, which also corresponds to the π -electron cloud thickness of aromatic hydrocarbon rings [25]. The d-spacings for the transmission data are found in Table IV. The wide-angle spacings are consistently greater in transmission than in reflection, thus indicating a difference in morphology parallel and perpendicular to the plane of the film. This difference in the spacing exists for each polypyrrole/anion system. The Van Der Waal's length for each counterion was calculated and is also given in Table IV [26]. The various sizes of the anions correspond to the d-spacings given by the small-angle peak. Wegner has reported a similar relationship for polypyrrole/tenside materials [27]. Further studies by Wernet and coworkers have led to a hypothetical model where the stacks of polypyrrole chains between the

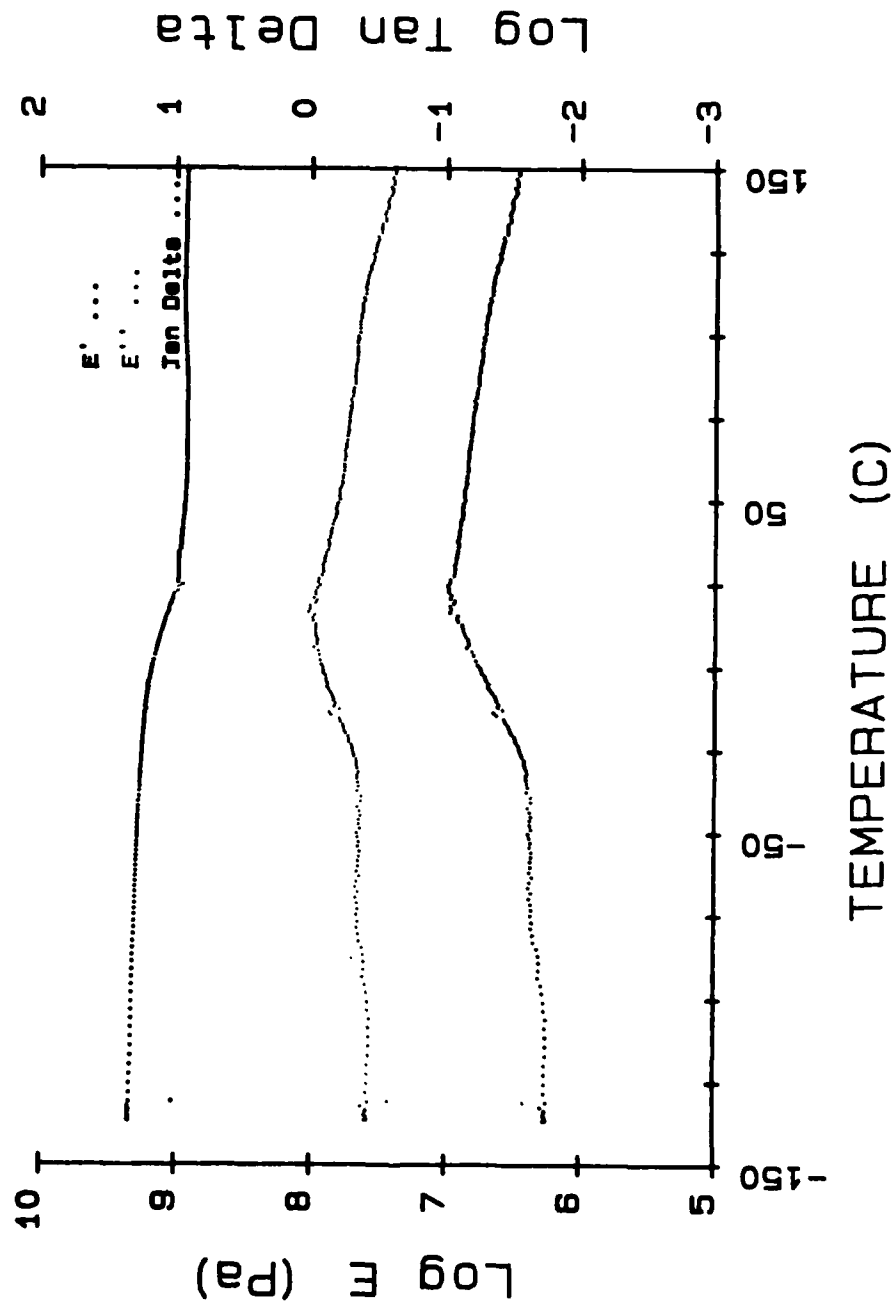


Figure 5. Rheovibron Plot of E', E'', and Tan Delta vs. Temperature for PP+OTs (E_{App} = 5V).

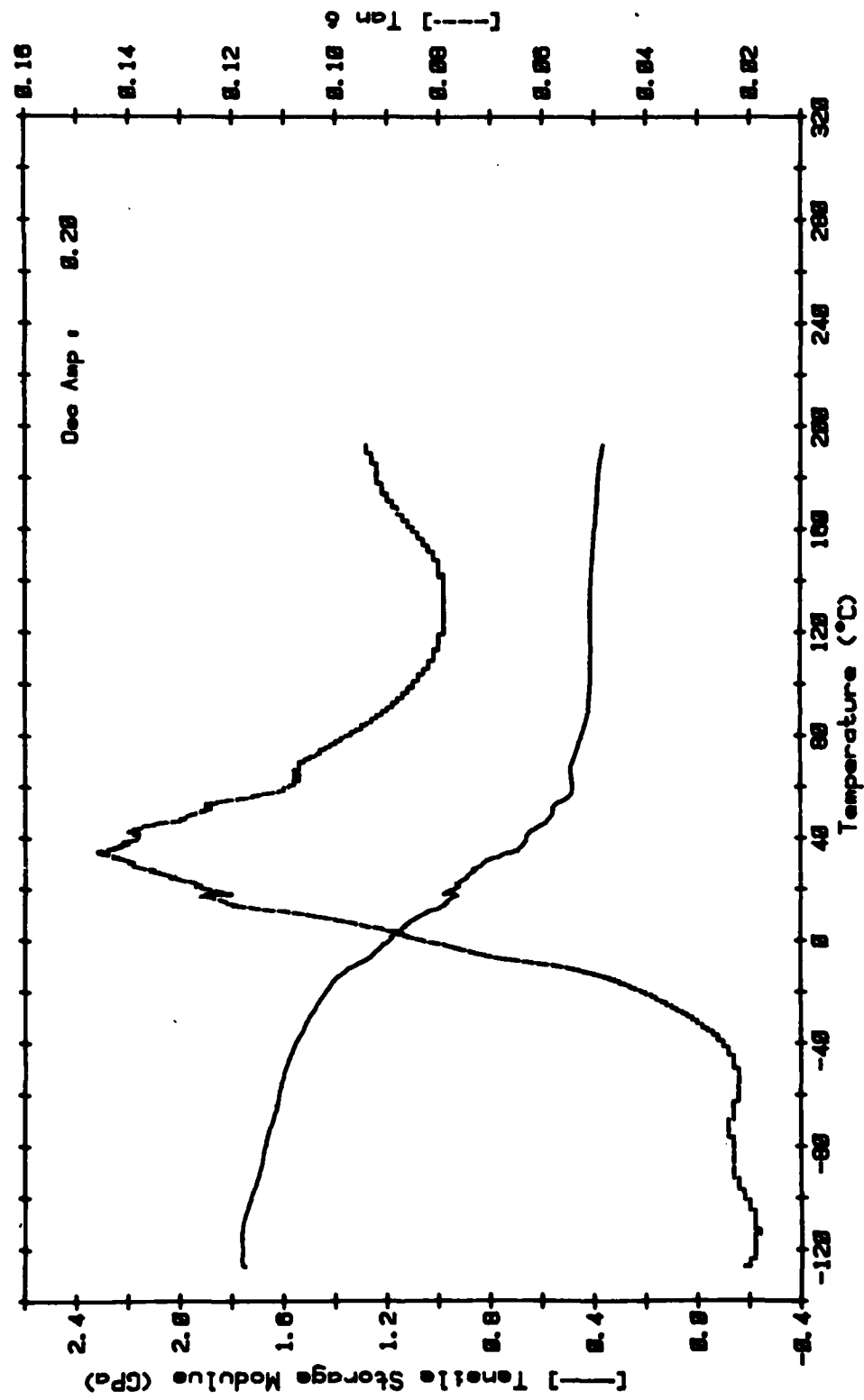


Figure 6. DMA Plot of E' , and Tan Delta vs. Temperature for PP+OTs ($E_{App} = 5V$).

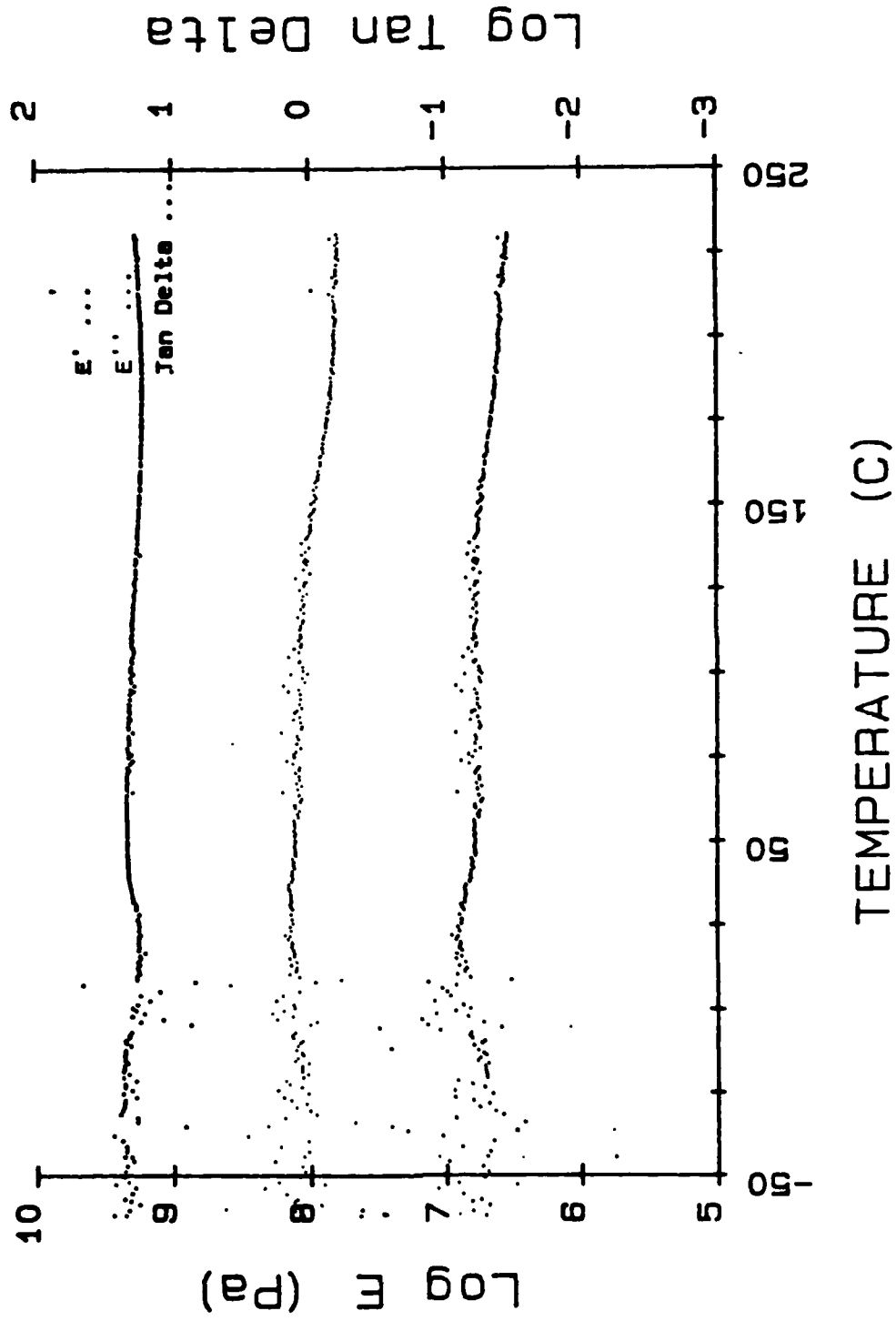


Figure 7. Rheovibron Plot of E', E'', and Tan Delta vs. Temperature for PP+/OTs Showing High Temperature Response.

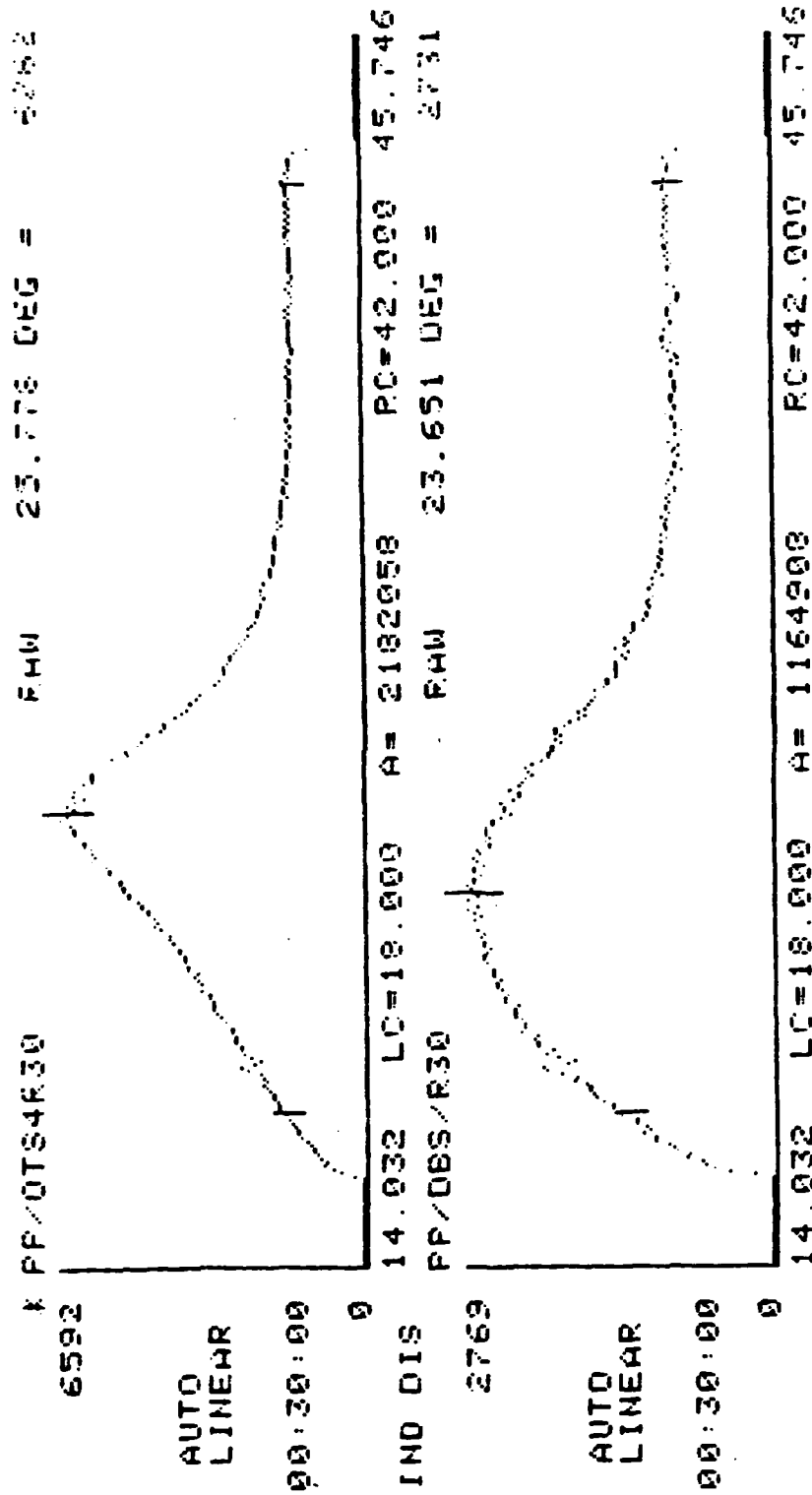


Figure 8. Reflection X-ray Data (Intensity vs. 2θ) Comparing PP+/OTS and PP+/DBS.

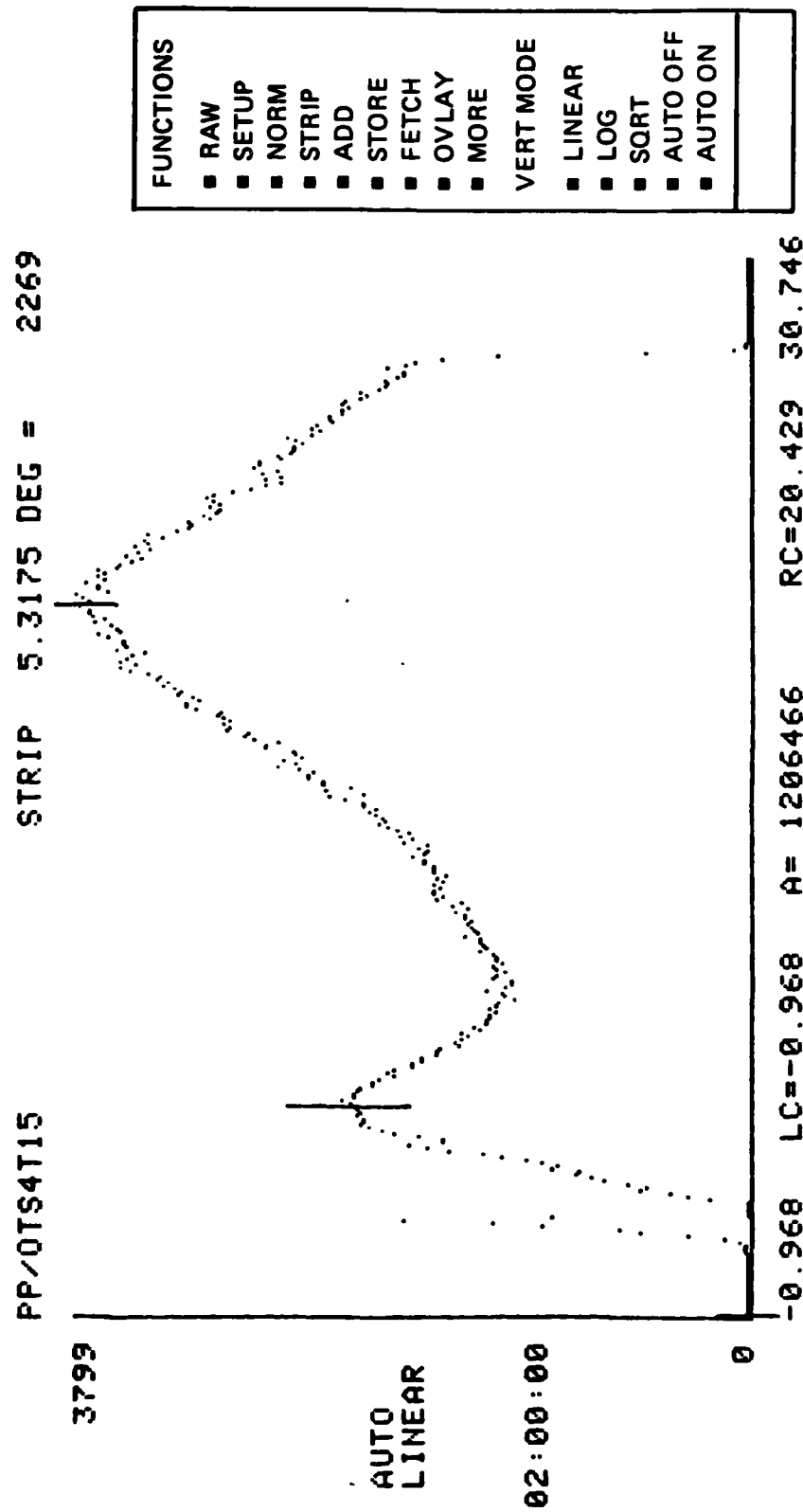


Figure 9. Transmission X-ray Data (Intensity vs. 2θ) for PP+/OTs- (Low Current Density).

TABLE III. SUMMARY OF X-RAY DATA IN THE REFLECTION MODE

<u>ANION</u>	<u>2θ</u>	<u>$d\text{ (\AA)}$</u>
OTs	25.778	3.45
BS	24.635	3.61
EBS	25.079	3.55
DBS	23.651	3.76
ClO ₄	25.143	3.54

TABLE IV. SUMMARY OF X-RAY DATA IN THE TRANSMISSION MODE

<u>ANION</u>	<u>VAN DER WAALS LENGTH (Å)</u>	<u>2 θ</u>	<u>d (Å)</u>	<u>2 θ</u>	<u>d (Å)</u>
OTs	12.1	5.317	16.62	20.429	4.35
BS	11.4	6.397	13.82	22.714	3.92
EBS	12.6	5.254	16.82	21.413	4.15
DBS	24.8	3.413	25.9	19.476	4.56
ClO₄	8.6	7.508	11.77	22.111	4.02

tenside ion double layers are postulated to be analogous to the structure of radical cation salts of simple arenes [28, 29].

The anisotropy that is indicated by the difference between the reflection and transmission modes can be more clearly seen by comparing the data on the same 2 θ scale and calculating the integral breadth which is equivalent to area of the peak divided by the maximum intensity for each. In addition to the obvious peak shift there is also a broadening in the transmission mode. The integral breadths were calculated and found to be 4.24 degrees for the reflection mode and 6.0 degrees for the transmission mode. This indicates an increase in order normal to the plane of the film (reflection mode) compared to within the film plane (transmission mode).

An approximation of the extent of order can be calculated by using the Debye-Scherrer equation [34]. Table V contains a list of the crystallite sizes and the integral breadths from which they were derived. The PP⁺/DBS⁻ material had less than half the average crystallite size of PP⁺/OTs⁻, thus indicating a significantly less ordered structure. This decrease in order was reflected in the poorer mechanical behavior of the PP⁺/DBS⁻ system. The difference in order that was seen among the anions was found to be primarily a function of the synthesis current density. For example, A PP⁺/OTs⁻ film prepared at 6V and 7.4 mA/cm² showed the same extent of broadening in the wide-angle x-ray peak that was seen for PP⁺/DBS⁻ made at 4V and 2.3 mA/cm². Films compared at the same current density for the tosylate and perchlorate anions show a small difference in the extent of order (see Table V). This suggests that the size and shape of the anion will affect the extent of order and consequently the mechanical behavior of the polymer. One must remember that oxidized polypyrrole is amorphous and any order that exists is short ranged (30 Å) at best.

The structure of neutral polypyrrole has been proposed by Geiss & Street as chains of pyrrole rings (mostly α -bonded) lying coplanar and separated by the Van Der Waals radii of the hydrogens within the plane and by the π -electron cloud thickness of aromatic groups through the plane [24]. The anions in conductive polypyrrole are reported to be intercalated between the chains within the plane [25]. Based on these statements a model of conductive polypyrrole with tosylate as the anion is shown in Figure 10. In this model the chain spacing in the plane without the anion is determined to be 4.8 Å. The observed wide-angle spacing within the plane was 4.35 Å for PP⁺/OTs⁻. With the anion the spacing is calculated to be 16.9 Å. The observed low-angle spacing within the plane was 16.6 Å. The observed wide-angle spacing through the plane was 3.45 Å compared to 3.41 Å given in the literature [25]. Thus, the structural model of conductive polypyrrole given in Figure 10 fits reasonably well with the experimental data.

TABLE V. LIST OF CRYSTALLITE SIZES AND INTEGRAL BREADTHS.

	<u>β_i (R)</u>	<u>D</u>	<u>β_i (T)</u>	<u>D</u>
PP+ / OTs-	4.24°	22.4 Å	6.0°	15.7 Å
PP+ / ClO4-	5.75°	16.5 Å	6.5°	14.5 Å
PP+ / DBS-	8.75°	10.8 Å	5.42°	17.3 Å

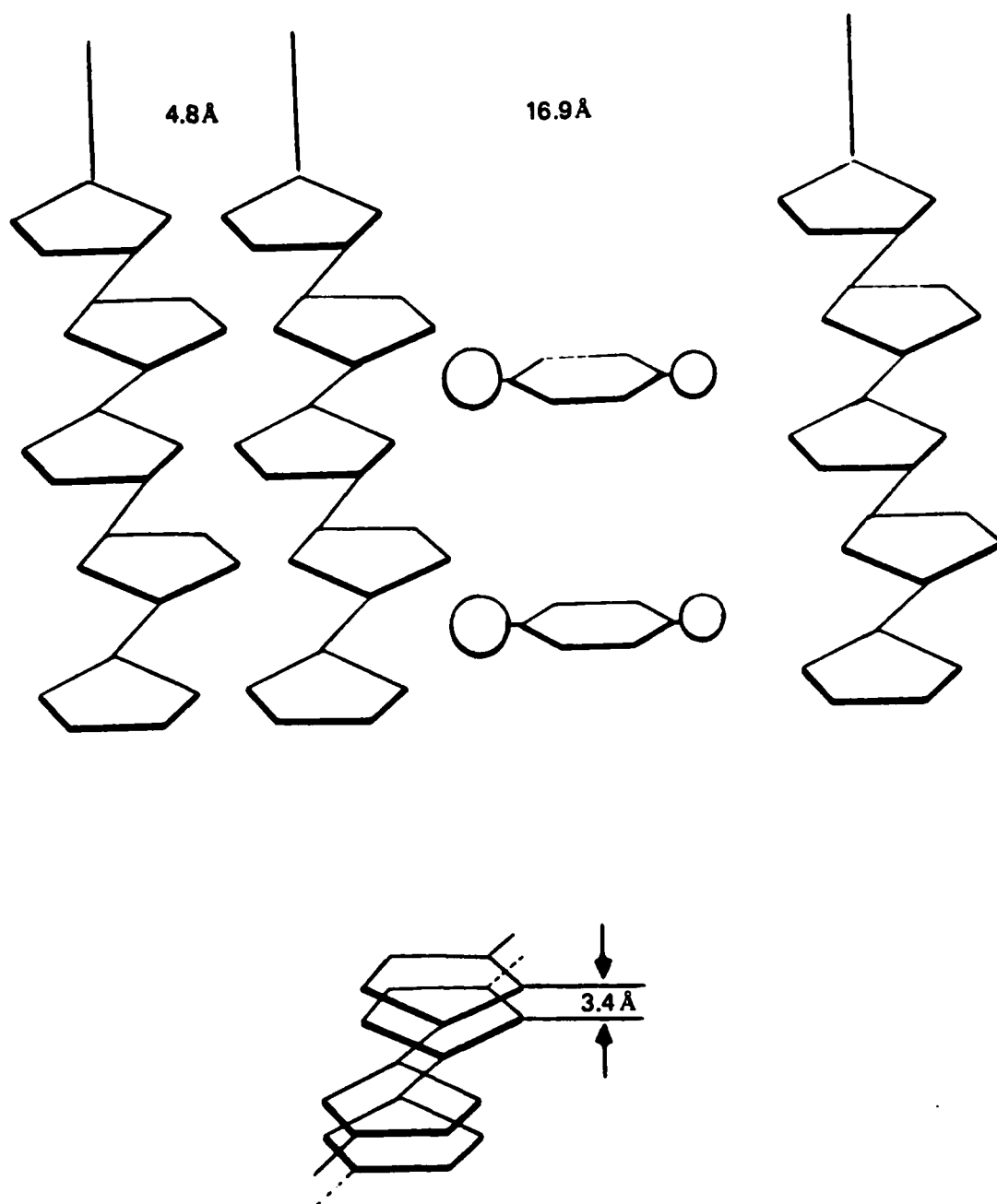


Figure 10. Model of PP+/OTs Based on the Van Der Waals Radii of the Atoms.

CONCLUSIONS

The synthesis, physical and mechanical properties, and structure of oxidized, electrically conductive polypyrrole have been studied and relationships have been investigated. The composition of PP^+/OTs^- was found to change with the synthesis potential. Elemental analysis showed an increase in the sulfur/nitrogen ratio upon increasing the synthesis potential. This indicates an increase in the anion content with synthesis potential. The ultimate tensile strength of PP^+/OTs^- was found to decrease as the synthesis potential and current density were increased during the preparation. The tosylate anion showed the best mechanical behavior of all of the polypyrrole/anion systems investigated in this study. In support of this result the tosylate anion also exhibited the most order structure as determined by x-ray diffraction analysis. This effect was due not only to the anion but to the synthesis current density as well. A higher synthesis current density yielded a less ordered material. The strain to failure was found to be less for PP^+/OTs^- synthesized under dry box conditions in agreement with previous findings in the literature. The mechanical properties of PP^+/OTs^- were dependent on the preparation conditions and the optimum properties are realized at the lower synthesis potentials and current densities. The optimum tensile strength and modulus of non-dry-box prepared PP^+/OTs^- were 10589 PSI [73 MPa] and 2.08×10^5 PSI [1.43 GPa]. Strain-to-failure ranged from 0.08 to 0.42.

Reflection and transmission x-ray diffraction of all of the PP^+ /anion materials showed a difference in d-spacing and order exists perpendicular and parallel to the plane of the films, thus indicating a non-homogeneous structure. Reflection x-ray data for PP^+/OTs^- indicated a d-spacing normal to the plane of the film that corresponded to the π -electron cloud thickness of pyrrole rings (3.41 Å). Transmission x-ray data indicate a larger spacing and less order within the plane of the film for all polypyrrole/anion systems. D-Spacings for the low-angle peaks correspond to the Van Der Waals size of the anion. The experimental data from the x-ray studies fit reasonably well to the proposed model.

Examination of the dynamic mechanical behavior revealed a small change in the tensile storage modulus (E') at approximately 30°C independent of the dopant anion. This small change in the modulus is most likely due to a slight movement of a short segment of the polypyrrole backbone that is similar to the secondary transition exhibited by amorphous polymers.

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